

Miscibility in Crystalline/Amorphous Blends of Poly(3-hydroxybutyrate)/DGEBA

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ABSTRACT: A differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS) study of miscibility in blends of the semicrystalline polyester poly(3-hydroxybutyrate) (PHB) and amorphous monomer epoxy DGEBA (diglycidyl ether of bisphenol A) was performed. Evidence of the miscibility of PHB/DGEBA in the molten state was found from a DSC study of the dependence of glass transition temperature (T_g) as a function of the blend composition and isothermal crystallization, analyzing the melting point (T_m) as a function of blend composition. A nega-

tive value of Flory–Huggins interaction parameter χ_{PD} was obtained. Furthermore, the lamellar crystallinity in the blend was studied by SAXS as a function of the PHB content. Evidence of the segregation of the amorphous material out of the lamellar structure was obtained. © 2013 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2013**, *51*, 680–686

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INTRODUCTION In the field of developing novel materials, the blending of polymers has given a new direction to research efforts. Improvements in mechanical properties, an increase in service life and the optimization of cost are goals pursued by the use of blends in technological applications. Polymer blends are combinations of at least two polymeric components that are miscible on a molecular scale or form immiscible or phase-separated heterogeneous multiphase systems. The degree to which the properties of a blend can be modified is believed to depend on the miscibility of the polymer pair used in blending. From a physical perspective, miscibility connotes homogeneity down to the molecular level.¹ To determine the miscibility of polymer blends, the existence of a single glass transition temperature is usually exploited. The glass transition temperature is measured by experimental techniques such as differential scanning calorimetry (DSC) or dynamic mechanical analysis. However, both experimental tools are sensitive only to heterogeneities larger than approximately 50 nm in domain size,² producing a limitation to measurements. Interestingly, a system that is determined to be miscible according to the results obtained by one technique can exhibit some heterogeneity when studied using another technique.³ Generally, it is observed that miscible blends exhibit transparency. Hence, the immiscibility of a blend is readily apparent because phase separation causes light scattering or limited transparency. However,

because domains can be smaller than the wavelength of light or can have similar refractive indices, mere visual inspection is not enough to confirm the miscibility of a blend.⁴ Moreover, if a component in the blend is crystallizable, then the samples can be opaque at temperatures below the melting point.

In the scenario presented, the interest in research on polymer blends has been directed toward systems in which at least one of the components is crystallizable. Attention has focused on the different morphologies resulting from the crystallization of the melt-miscible phase of semicrystalline/amorphous blends.⁵ The type of polymers used as components in blends and that generally show a high degree of crystallinity are biodegradable polymers obtained from natural resources.^{5,6} Poly(3-hydroxybutyrate) (PHB) is one of the most studied polymers as a component for blending, and efforts have been dedicated to reducing the high brittleness of this material attributed to its high crystallinity.^{7–9}

The microbially synthesized (PHB) is an environmentally friendly polymer. The interest in this polymer is based on its biodegradability and biocompatibility properties. However, PHB is semi-crystalline, isotactic and has a relatively high crystallinity, which makes it a tough and quite brittle material. Although PHB has exhibited good characteristics in some cases compared to conventional polymers, such as a

resistance of 35.80 MPa or a modulus of elasticity of 3.04 GPa, and has been demonstrated to be suitable for the use in packaging for food conservation,¹⁰ the fragility and the very low resistance to thermal degradation during processing has currently limited the practical applications of neat PHB. Therefore, research efforts have been focused on mixing PHB with different polymers.¹¹

However, epoxy is a thermoset polymer that is widely used as a matrix in polymer composites or in the formation of interpenetrating networks. The blending of semicrystalline polymers with epoxy has been scarcely addressed in the literature.^{6,12} However, it is important to understand the phenomena involved during the curing of epoxy/semicrystalline blends because the final morphology of the material depends on the blend's initial miscibility and on whether the material crystallizes during the curing. Thus, the first step to reaching a complete understanding of the structure of semicrystalline/epoxy blends is to determine the initial miscibility of the blends before developing the curing process. DGEBA (diglycidyl ether of bisphenol A) monomer is one of the materials that is most often used to develop epoxy networks. Therefore, the study of PHB/DGEBA blends is essential to the study of other blends. From a thermodynamic perspective, it is very important to study the blend of a semicrystalline polymer (PHB) with DGEBA monomer because that this blend is classified as an intermediate state between a polymer/diluent blend and polymer/polymer blend.

The aim of this work was to obtain information about the miscibility of PHB/DGEBA blends, study the influence of DGEBA on the melting point of PHB and correlate the results with information about morphological changes in the lamellar structure of PHB using small-angle X-ray scattering (SAXS).

EXPERIMENTAL

Samples Preparation

A PHB powder with the trade name Biocycle® was supplied by Industrial (Brazil). Epoxy DGEBA monomer (diglycidyl ether of bisphenol A) was supplied by Hunstman (Araldite MY 790). For DSC measurements, pure PHB, DGEBA, and blend samples with the following PHB/DGEBA ratios in weight 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 20/80, and 0/100 of total mass of approximately 20 mg were poured into DSC pans. The samples in the DSC pans were melted in the calorimeter before the thermal scans were run to ensure homogeneity. Different tests were performed to assure that the procedure was repeatable. For SAXS measurements, blend samples with the following PHB/DGEBA ratios in weight 100/0, 90/10, 80/20, 70/30, 60/40, and 50/50 were melted at 180 °C. A homogeneous solution was observed at that temperature. Then, the samples were rapidly cooled in a freezer. Afterward, the samples were poured in modified DSC pans with kapton windows suitable for SAXS measurement.

DSC Measurements

DSC measurements of pure PHB, DGEBA, and blends PHB/DGEBA were performed using a Q20-TA INSTRUMENTS dif-

ferential scanning calorimeter. The calorimeter was calibrated with respect to temperature and heat flow using indium and mercury as reference materials. All measurements were performed under an argon atmosphere with a constant flux of 50 mL/min.

Measurement of Glass Transition Temperature

Glass transition temperature (T_g) measurements were performed by means of a heating/cooling/heating cycle. Each measurement began by heating from room temperature to 190 °C at 10 °C/min (first heating). Then, the samples were kept at 190 °C for 60 s to remove the thermal history. Afterward, the samples were cooled to -40 °C at 10 °C/min rate and reheated to 190 °C at 10 °C/min rate (second heating). The T_g was obtained from the midpoint of the slope in the heat step from the curves of heat flow as a function of temperature (thermograms) of the second heating.

Isothermal Crystallization

Isothermal crystallization was performed by a first heating from room temperature to 190 °C at a rate of 10 °C/min. The samples were kept at 190 °C for 120 s to remove the thermal history; they were then rapidly cooled to avoid crystallization (cooling rate ≈ -60 °C/min) to the crystallization temperatures (T_c) and finally kept at T_c for 1200 s to induce the crystallization process. The selected crystallization temperatures were between 40 and 125 °C. The melting temperature (T_m) of each crystallized sample was then measured using a second heating from T_c up to 190 °C at 10 °C/min. The T_m was determined by the endothermic peak, selecting the minimum as the best value.

SAXS Measurements

SAXS measurements were performed at the Brazilian Synchrotron Light Laboratory (LNLS) CNPEM/MCT, line SAXS 1 Campinas, Brazil. A wavelength of $\lambda = 1.55$ Å was selected for the monochromatic beam used in the experiments. The low-angle scatter was recorded for scattering vector values q ($q = (4\pi/\lambda) \sin \theta$), where 2θ is the scattering angle, between $q_{\min} = 0.016$ (Å⁻¹) to $q_{\max} = 0.300$ (Å⁻¹) using a position sensitive detector for the small-angle region located at a distance of 627 mm from the sample. The measurements were performed using a two-dimensional (2D) detector with a spatial resolution of 172 μm. The 2D scattering profiles were radially averaged and converted to 1D data using the program FIT2D V12.077. The experimental small-angle scattering curves were normalized by the integrated incident beam intensity.

RESULTS AND DISCUSSION

Glass Transition Temperature (T_g)

DSC thermograms for all composition studies are shown in Figure 1(a). As shown, for all compositions, a single T_g (pointed with arrows in the Figure) was observed. In Figure 1(b), T_g values as a function of PHB content in the blend are shown. As shown, a systematic shift in T_g to higher temperature is observed when the PHB content in the blends is increased. Furthermore, in the thermogram obtained from the measurement of pure PHB [see inset in Fig. 1(a)], a

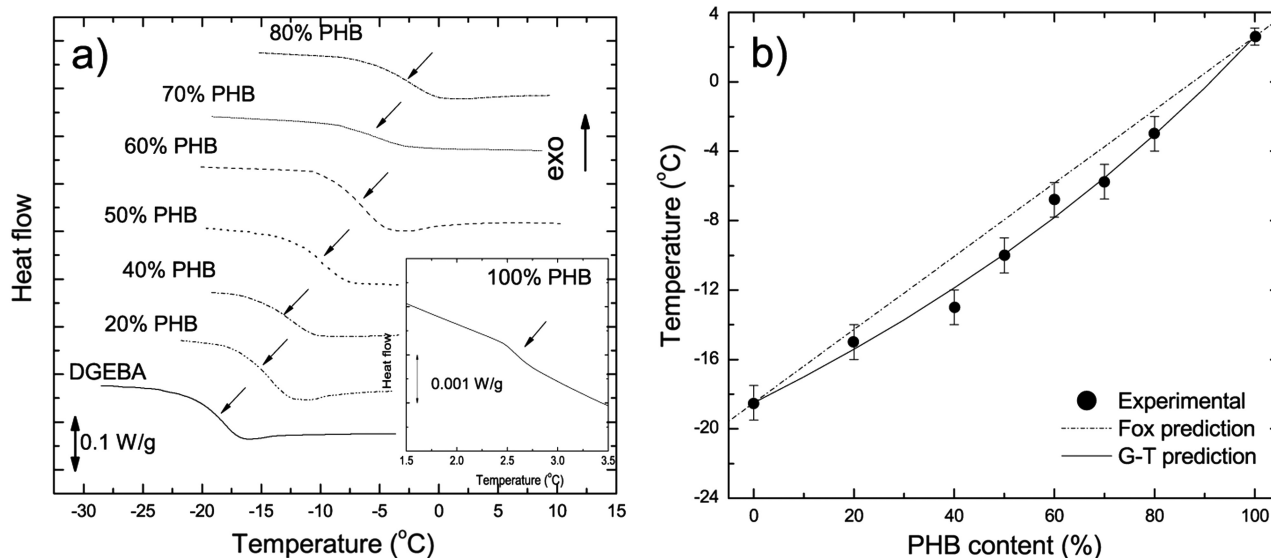


FIGURE 1 (a) DSC thermograms of pure DGEBA, PHB/DGEBA blends and pure PHB (in inset). The arrows indicate the glass transition temperature T_g . (b) T_g as function of PHB content in blends. Fox prediction (dot line) and Gordon-Taylor equation best fit (line) to the experimental result.

higher T_g (2.6 °C) than those of the composites (between -15 and -3 °C) and pure DGEBA ($T_g = -18.5$ °C) was found. The thermogram of pure PHB exhibits similar characteristics to that observed by de Lima et al.⁵

In the literature, different models have been proposed to predict the variation in T_g as a function of blend composition.¹³ The model most commonly used is described by the Fox equation^{9,14}:

$$\frac{1}{T_g} = \frac{w_D}{T_{gD}} + \frac{w_P}{T_{gP}} \quad (1)$$

where w_D and w_P are the weight fractions of DGEBA and PHB pure components, respectively, and T_{gD} and T_{gP} are the glass transition temperatures of the same pure components mentioned. However, as shown in Figure 1(b), the Fox equation (dotted line) does not exactly predict the experimental results obtained for T_g as a function of the PHB content in the blends under study. A deviation from linearity is observed.

To take into account the deviation from linearity observed in the experimental results for T_g as a function of PHB content, the Gordon-Taylor equation¹³ seems to be more adequate because it can describe such deviations from linearity, both positive and negative:

$$T_g = \frac{w_D T_{gD} + k w_P T_{gP}}{w_D + k w_P} \quad (2)$$

where w_D , w_P , T_{gD} , and T_{gP} were defined above; k is an adjustable parameter that is often related to the strength of intermolecular interactions between the components of a blend. A fit of the experimental results using eq 2 is also depicted in Figure 1(b). The k parameter (0.68 ± 0.04) was

obtained. This value is higher than that obtained by Guo for blends of DGEBA with phenolphthalein poly(ether ether sulfone) (PES-C), 0.31.¹⁴ However, the value obtained is lower than that reported by Vanden et al. for blends of DGEBA with polycaprolactone (PCL) of different molecular weights: 1.10 and 1.03 for the highest and lowest molecular weights, respectively.¹⁵

The results described above could suggest that PHB and DGEBA are miscible over the whole composition range studied. However, according to the literature,¹⁶ the miscibility of a binary blend can be readily determined by measuring the T_g of the blend whenever the difference in the glass transition temperatures between the two components of blends exceeds 20 °C. In this study, the difference between the T_g of PHB and DGEBA is approximately 21 °C, and although it would be over the limit mentioned above, the difference obtained is close to this value; therefore, it is necessary to confirm the miscibility value using another experimental method. It is important to note that all blends studied are transparent just above the melting point of PHB, which is also an indication that PHB and DGEBA are miscible in the molten state.

Moreover, there are reports in the literature supporting the idea that it is incorrect to establish the criteria for miscibility only on the basis of the presence of a single T_g because there are examples of miscible polymer blends characterized by two glass transitions.¹⁷⁻¹⁹ To gain more information about miscibility, an isothermal crystallization study determining the melt temperatures (T_m) as function of blend composition was performed by DSC. The obtained melt temperatures are shown in Figure 2(a) as a function of the crystallization temperature (T_c) for all compositions studied. As shown, the T_m increases systematically with an increase in the crystallization temperature T_c for all blends studied. This trend can be

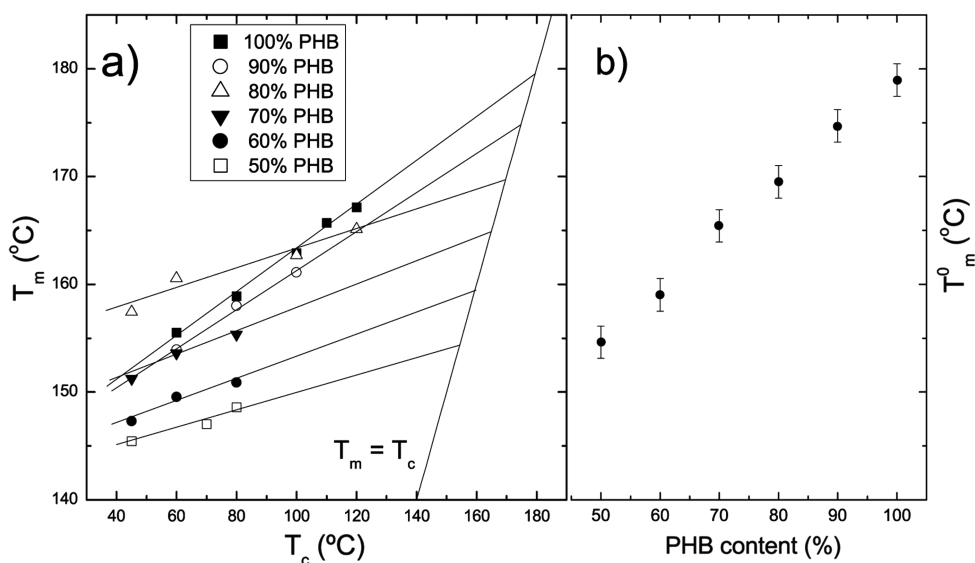


FIGURE 2 (a) Melting temperatures (T_m) as a function of the crystallization temperature (T_c) for the blend compositions studied by DSC. The value of T_m^0 (see text) is obtained from the plot of T_m as a function of T_c by extrapolating a linear fit of the experimental results for each blend composition studied until it intersects with the $T_m = T_c$ line. (b) T_m^0 as a function of PHB content in blends.

explained in terms of thermodynamic mixing by the exothermic interaction between a crystalline and an amorphous polymer and in terms of kinetic or morphological factors such as crystal thickness and size. To remove the morphological effects, the equilibrium melting temperature (T_m^0) was derived using the Hoffman-Weeks equation²⁰:

$$T_m = \frac{T_c}{\gamma} + \left(1 - \frac{1}{\gamma}\right) T_m^0 \quad (3)$$

where γ is the ratio of the initial to final lamellar thickness. The value of T_m^0 is obtained from the plot of T_m as a function of T_c [Fig. 2(a)] by extrapolating a linear fit of the experimental results, for each blend composition studied, until it intersects with the $T_m = T_c$ line. γ can be estimated from the inverse of the slope of T_m versus T_c linear fit.

The values of T_m^0 obtained as a function of PHB content are shown in Figure 2(b). As shown, in the range of blend compositions studied, T_m^0 decreases from 179 to 154 °C as a function of the increase in the DGEBA content of the blends. The value of 179 °C for pure PHB is close to the value of 186.0 °C reported by Xing et al.⁷ Figure 2(a) shows that the slope of T_m versus T_c plot is higher for pure PHB and the 90/10 PHB/DGEBA blend with respect to the other blends. Changes in the slopes of T_m versus T_c have been observed in PHB blends^{8,9} and have been associated with a variation in γ .⁸

The reduction in the melting point observed when the PHB content in the blends decreases can be explained by taking into account the decrease in the chemical potential of the crystallizable polymer caused by the increment in the miscible diluent added. The dependence of the melting point depression as a function of only thermodynamic effects on the blend composition is given by the Flory-Huggins

theory.²¹ The Flory-Huggins interaction parameter χ provides information about the miscibility of blends or mixtures and can be determined using the melting equilibrium temperature using the Nishi-Wang approach,²² which is expressed as follows:

$$\frac{1}{T_m^0\left(\frac{P}{D}\right)} - \frac{1}{T_m^0(P)} = -\frac{RV_P}{\Delta H^0 V_D} \left[\frac{\ln \varphi_P}{m_P} + \left(\frac{1}{m_P} - \frac{1}{m_D} \right) \varphi_D + \chi_{PD} \varphi_D^2 \right] \quad (4)$$

where P represents PHB and D represents DGEBA, T_m^0 (P/D) and T_m^0 (P) are the equilibrium melting points of the blend and homopolymer, respectively, ΔH^0 is the heat of fusion for the 100% crystallizable component, V_D and V_P are the molar volumes of the repeat units of the DGEBA (noncrystallizable) and PHB (crystallizable) component, respectively, φ_D and φ_P are the volume fraction, m_P and m_D are the degree of polymerization, and R is the universal gas constant ($R = 1.987$ cal/mol K). In eq 4, χ_{PD} is the Flory-Huggins interaction parameter of the PHB/DGEBA blends studied.

Rearranging the eq 4, a β parameter can be obtained:

$$\beta = \left[\frac{1}{T_m^0\left(\frac{P}{D}\right)} - \frac{1}{T_m^0(P)} \right] \frac{\Delta H^0 V_D}{RV_P} + \frac{\ln \varphi_P}{m_P} + \left(\frac{1}{m_P} - \frac{1}{m_D} \right) \varphi_D \quad (5)$$

$$\beta = -\chi_{PD} \varphi_D^2$$

Therefore, according to eq 5, the plot of β as a function of φ_D^2 should be linear with slope $-\chi_{PD}$. Figure 3 depicts a plot of β versus φ_D^2 obtained using the values of T_m^0 from Figure 2(b) and the following parameters: $V_D = 289.7$ cm³/mol and $V_P = 75$ cm³/mol, both volumes calculated according to the Fedors method of group contribution^{23,24}; $\Delta H^0 = 3001$ cal/mol,⁹ $m_P = 1806.2$ and $m_D = 1$ (m_P and m_D were calculated from the ratio of the molar volumes of PHB and DGEBA to a

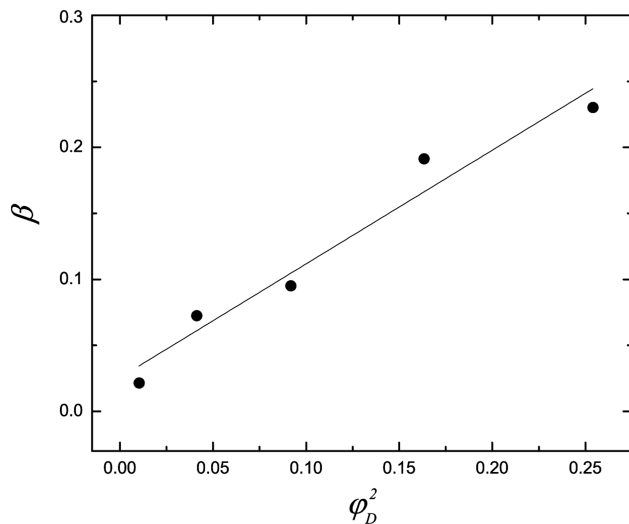


FIGURE 3 β as a function of φ_D^2 , obtained using the values of T_m^0 presented in Figure 2(b). See text.

reference volume V_0 . In this work, V_0 was assumed to be the molar volume of DGEBA²⁵).

As can be seen, a monotonous increment in β as a function of φ_D^2 is observed. A linear regression, shown in Figure 3, was performed. From the slope of the linear regression, a value of $\chi_{PD} = -0.86 \pm 0.10$ was obtained. The negative value of χ_{PD} suggests that DGEBA and PHB are miscible in the molten state. A similar negative value of -0.81 has been reported for χ in miscible blends of DGEBA with another semicrystalline biodegradable polymer, poly(L-lactide) PLLA.⁶

Morphology

The lamellar periodicity of PHB/DGEBA blends was studied using the SAXS experimental technique. The results obtained for pure PHB and PHB/DGEBA blends are shown in Figure 4 as Lorentz plots ($I(q)q^2$ versus q).²⁶ As can be seen, there is a maximum for all samples studied; the maximum is asso-

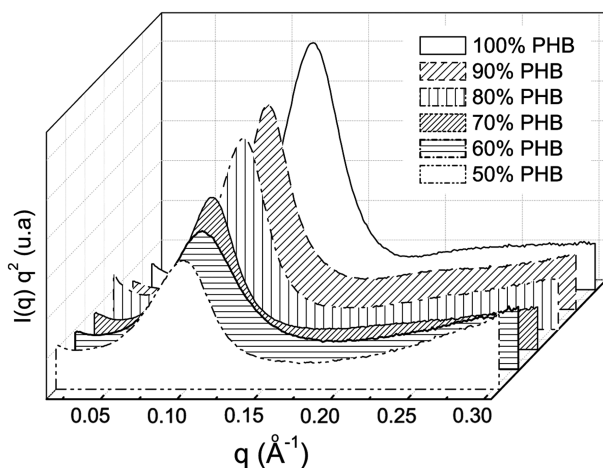


FIGURE 4 Lorentz representation for scattering vector between 0.016 and 0.300 \AA^{-1} as a function of PHB content in blends studied by SAXS.

ciated with the long period between the centers of adjacent lamellae.

$I(q)q^2$ versus q curves were analyzed by the normalized 1D correlation function $\alpha(r)$, which corresponds to the Fourier transformation of the Lorentz plot.

$$\alpha(r) = \frac{\int_0^\infty q^2 I(q) \cos(qr) dq}{\int_0^\infty q^2 I(q) dq} \quad (6)$$

Because the integrals must be evaluated between zero and infinity, it is necessary to extrapolate the scattering intensity at high and low values of q . Extrapolation to low values of q has been performed using the Vonk model using CORFUNC code,²⁷ where it is assumed that the dispersion profile is defined as follows:

$$I(q) = H_1 - H_2 q^2 \quad (7)$$

where H_1 and H_2 are constants.

Extrapolation to high values of q was performed considering Porod's Law:

$$I(q) = I_b + K/q^4 \quad (8)$$

where I_b is the intensity of the background and K is the Porod constant.

Assuming an ideal lamellar structure with interlamellar spacing (average long period) L and formed by a crystalline component with thickness l_c and an amorphous component with thickness l_a , through the analysis of the correlation function L , l_c and l_a can be determined.²⁸ In Figure 5, the 1D correlation functions for all blends studied are shown, indicating how the L and l_i ($i = 1, 2$) parameters are obtained. l_i represents l_c or l_a , depending on the sample. If l_c is known, then l_a can be calculated from the relationship $L = l_c + l_a$ and vice

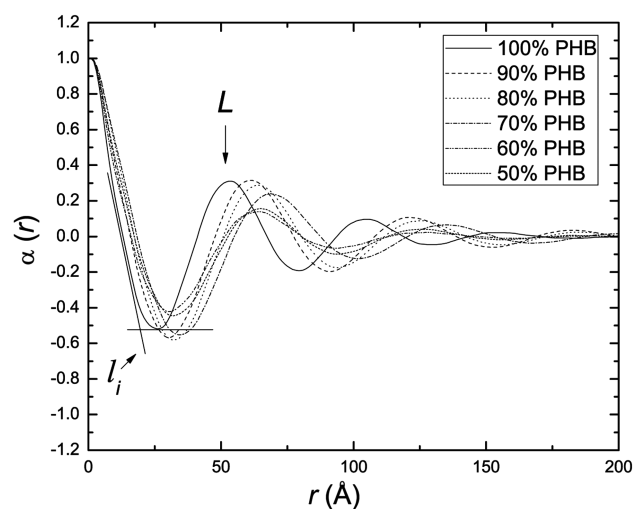


FIGURE 5 Schematic presentation of a 1D correlation function $[\alpha(r)]$ and the morphological parameter determined: long spacing (L) and l_i ($i = 1, 2$). See text).

TABLE 1 L , l_1 , and l_2 obtained from the 1D Correlation Function (Fig. 5) and the Values of l_1/L and l_2/L and ϕ_c obtained from DSC Measurements

PHB Content (%)	L (Å)	l_1 (Å)	l_2 (Å)	l_1/L (%)	l_2/L (%)	ϕ_c (%)
100	53.0 (±0.2)	13.0 (±0.1)	40.0 (±0.1)	24.5	75.5	58.8
90	60.0 (±0.3)	19.8 (±0.5)	40.2 (±0.7)	33.1	66.9	46.7
80	63.0 (±0.3)	21.4 (±0.1)	41.6 (±0.2)	34.0	66.0	38.9
70	68.0 (±0.3)	25.1 (±0.2)	42.9 (±0.2)	36.9	63.1	38.8
60	63.0 (±0.3)	18.0 (±0.1)	45.0 (±0.1)	28.6	71.4	29.7
50	64.0 (±0.3)	19.2 (±0.1)	44.8 (±0.1)	30.0	70.0	18.7

versa. The linear degree of crystallinity within the lamellar structure X_c^{SAXS} is obtained from the following expression ²⁹:

$$X_c^{SAXS} = \frac{l_c}{L} \quad (9)$$

To determine l_a and l_c from the l_i values obtained by SAXS, some considerations should be taken into account. From Babinet's reciprocity theorem, the electronic density of a two-phase structure can be exchanged without affecting the correlation function.²⁸ The assignment of l_i as l_c or l_a was performed with the help of the results from DSC measurements. From DSC, the bulk degree of crystallinity of the blend ϕ_c was obtained and compared with the linear degree of crystallinity X_c^{SAXS} . X_c^{SAXS} is greater or equal than ϕ_c because not all the morphology of the blend is lamellar.²⁹ Then, the assignment of l_i as l_c or l_a in the PHB/DGEBA blends was performed by considering the value that satisfies $X_c^{SAXS} \geq \phi_c$. For blends with a 50/50 composition, the ratio of both l_i are greater than ϕ_c ; in this case, the assignment was performed by considering the monotonic behavior of l_c . X_c^{SAXS} was obtained from eq 9, and ϕ_c was calculated using the equation derived by Huo et al.³⁰

$$\phi_c = \frac{\frac{X_c \rho_c}{\rho_c + \frac{W_D - X_c}{\rho_a} + \frac{1 - W_D}{\rho_D}}}{\rho_c + \frac{W_D - X_c}{\rho_a} + \frac{1 - W_D}{\rho_D}} \quad (10)$$

where ρ_c and ρ_a are the densities of 100% crystalline PHB and amorphous PHB ³¹ ($\rho_c = 1.260 \text{ g/cm}^3$, $\rho_a = 1.177 \text{ g/cm}^3$), ρ_D is the density of DGEBA ($\rho_D = 1.175 \text{ g/cm}^3$) and X_c is the crystallinity of the blend:

$$X_c = \frac{\Delta H_m^P}{\Delta H^0} \quad (11)$$

where ΔH_m^P is the heat of fusion obtained from the DSC scan of each sample studied.

The results for L , l_1 , and l_2 obtained from the 1D correlation function and the values of l_1/L and l_2/L and ϕ_c are presented in Table 1.

It is worth mentioning that considering the above discussion and the results shown in Table 1, it was concluded that l_2 corresponds to l_c .

In Figure 6, the degree of crystallization obtained by SAXS (X_c^{SAXS}) and by DSC (ϕ_c) is shown. It can be observed that X_c^{SAXS} is between 0.62 and 0.72 and shows an increase to 0.75 for pure PHB. ϕ_c is observed to increase as a function of PHB content, from 0.18 for samples with 50% PHB to 0.38 for samples with 70% PHB. A similar value is measured for blends with 80% PHB. A further increment in ϕ_c is observed for a PHB content above 70%. Pure PHB shows a value of $\phi_c = 0.58$.

The relation ϕ_c/X_c^{SAXS} was calculated and is also shown in Figure 6. A value of ≈ 0.77 is obtained for pure PHB and decreases when the PHB content in the blend decreases. A value equal to 1 for this relation indicates that all of the amorphous phase in the blend is located in the lamellar structure. However, if this relation results in a value lower than 1, interfibrillar or interspherulitic segregation is expected.²⁹ The change in the slope of the relation ϕ_c/X_c^{SAXS} as a function of PHB content observed for PHB contents below 70% indicates a higher degree of segregation for this PHB content range. This result is according to the fact that a diminution in the amorphous phase thickness l_a is observed for PHB contents below 70% (see Table 1).

The thickness of crystalline component l_c increases when the PHB content decreases. The initial crystal thickness is given by ^{29,32}

$$l_g^* = \frac{2\sigma_e T_m^0}{\Delta H_{m/V}^0 (T_m^0 - T_c)} + \delta \quad (12)$$

where σ_e is the fold surface free energy, $\Delta H_{m/V}^0$ is the heat of fusion per unit volume of the pure PHB and δ is the minimum thickness that gives the necessary stability to form the crystal. δ can be considered to be negligible for small to moderate values of supercooling.²⁶ The final crystal thickness l_c is γ times the initial thickness l_g^* .

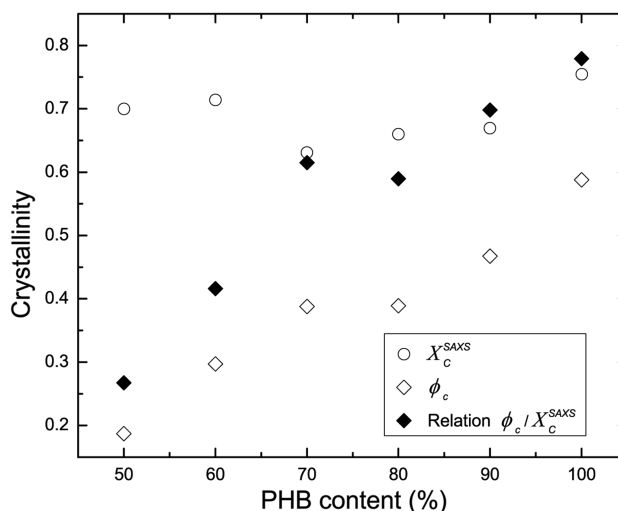


FIGURE 6 Degree of crystallization obtained from SAXS (X_c^{SAXS}) and DSC (ϕ_c) and relation ϕ_c/X_c^{SAXS} as a function of PHB content in the blends.

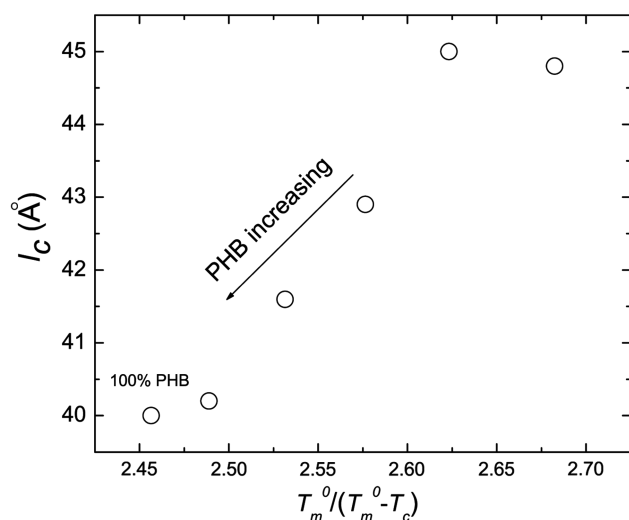


FIGURE 7 l_c as a function of $T_m^0 / (T_m^0 - T_c)$.

$$l_c = \gamma l_g^* \quad (13)$$

From eqs 12 and 13, it is possible to conclude that l_c can be modified in different ways—a change in σ_e , a change in σ or a modification in the degree of supercooling—because if T_c is held constant and T_m^0 changes with the increase in the noncrystallizable component, then the factor $T_m^0 / (T_m^0 - T_c)$ varies for different blends. A plot of l_c as a function of $T_m^0 / (T_m^0 - T_c)$ is shown in Figure 7. As can be seen, a linear behavior is observed until the sample reaches a composition of 60/40. In the 50/50 sample, a deviation from linearity is observed. This behavior indicates that the principal effect on l_c in the PHB/DGEBA blends could be associated with the variation in the degree of supercooling.

CONCLUSIONS

PHB/DGEBA blends were investigated using SAXS and DSC techniques. The blends were observed to be miscible over the entire composition range of DGEBA based on the reduction of the T_g as a function of the PHB content and on the negative value of the interaction parameter. The interaction parameter was obtained by analyzing the depression of the equilibrium melting temperature (T_m^0) as a function of the reduction in the PHB content of the blends from a thermodynamic perspective using the Nishi–Wang approach. The DGEBA introduces an amorphous component in the lamellae for contents less than 30%, but it is partially segregated from the lamellae for contents greater than 30%. An increase in the l_c parameter was observed when the PHB content decreased. This result was explained in terms of the reduction in the equilibrium melting temperature when the PHB content of the blends decreased.

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